Lean NO_x Traps - Microstructural Studies of Real World and Model Catalysts

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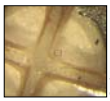
In order to design a thermally durable NO_x trap, there is a need to understand the changes in the microstructure of materials that occur during various modes of operation (lean, rich, and lean-rich cycles). This information can form the basis for selection and design of new NO_x trap materials that can resist deterioration under normal operation.

Microstructural Changes in Production Lean NO_x Traps on Aging



Two-Layer System:
- Pt-BaO-Al_2O_3 inner layer (dark orange)
- Rh-CeO_2-ZrO_2 outer layer (light orange)

TEM ion-milled thin foil specimen of cordierite "cross" from catalyst honeycomb, mounted in epoxy on graphite washer.

•Pulsator Aging

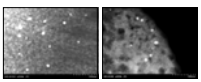
- Lean and rich aged samples showed that the sintering of platinum particles occurs during aging and that barium migrates into ceria-zirconia layer.
  - –Both of these factors reduce platinum-barium oxide surface area where NOx adsorption and reduction takes place during lean and rich cycles respectively.
- The stoichiometric aging also leads to the migration of barium into the ceria-zirconia layer, but the sintering of platinum is less severe.

•Dyno Aging

- The dyno aged samples showed extensive sintering of platinum and its migration in ceria-zirconia layer.
- The sintering of rhodium as well as the migration of barium into ceria-zirconia was also observed.
- These observation explain the deterioration in LNT performance.

•Passenger Vehicle (DISI Fleet) Aging

- The analysis of on vehicle evaluated samples after 32K km and 80K km showed that the bulk of precious metal sintering occurred in the early stages of on-vehicle aging



TEM of Inner Layer of LNTs after 30,000 km (left) and 82,000 km (right)

Model Catalysts

Model Catalysts were prepared by step-wise impregnation of commercial alumina:

•Catalyst A: 2%Pt-98%[10%CeO_2-ZrO_2-90% (2%La_2O_3-98%BaO•6Al_2O_3)]

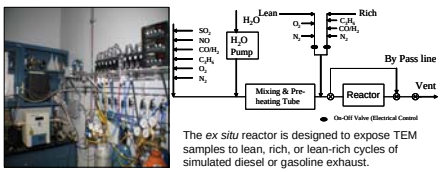
- Impregnate alumina with barium salts and thermally treat in air to obtain BaO•6Al_2O_3
- Impregnate BaO•6Al_2O_3 with Lanthanum salts and thermally treat in air to obtain 2%La_2O_3-98%BaO•6Al_2O_3
- Ball mill 2%La_2O_3-98%BaO•6Al_2O_3 with commercial CeO_2-ZrO_2
- Impregnate 10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO•6Al_2O_3) with Pt salts and thermally treat to obtain model NOx trap

•Catalyst B: Pt/Al_2O_3

- Impregnate alumina with Pt salts and thermally treat to obtain model NO_x trap

•Catalyst C: 2%Pt, 5%MnO_2-93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO.6Al_2O_3)]

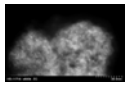
- Impregnate 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%BaO.6Al_2O_3)] with manganese salts and thermally treat to obtain model NOx trap



The *ex situ* reactor is designed to expose TEM samples to lean, rich, or lean-rich cycles of simulated diesel or gasoline exhaust.

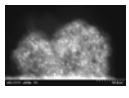
Aging Studies on *Ex Situ* Reactor

•Lean-Rich Cycle Aging (500°C, 4h) of Model Catalyst A [240s - 60s cycle]



•Fresh Sample

– Pt particles in 0.5 - 2.5-nm range



•After 4 hours

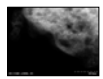
–Pt particles in 0.5 - 4.3-nm range

–Change in location

•Pt particle size change under various treatments to the model catalysts

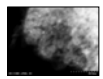
Model Catalyst	Fresh Sample[1]	Thermal Aging In Air (XRD of powder)	Lean Diesel Aging 500°C/4 h	Rich Diesel Aging 500°C/ 4 h	Lean/ Rich Cycle Diesel Aging 500 °C/4 h	
					60 s/5s	240 s/60 s
2% Pt / γ-Al_2O_3	0.8 – 2.0 nm (1.4 nm)	600°C, 3.4nm 700°C, 17.1nm 800°C, 26.1nm 900°C, 39.5nm	1.0 – 2.0[1] nm (1.5 nm)	2.0 - 4.0 nm	N/A	0.6 – 3.0 nm (1.5 nm)
2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	0.6 – 2.9 nm (1.4 nm)	600°C, 2.6 nm 700°C, 21.3nm 800°C, 37.2nm 900°C, 48.4nm	1.0 -2.0 nm	1.5 - 3.5 nm	0.5 – 4.3 nm (1.7 nm)	0.8 – 3.5 nm (1.7 nm)
2%Pt, 5%MnO_2-93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	0.7 – 2.6 nm (1.6 nm)	700°C, 20.7nm 800°C, 27.0nm 900°C, 34.0nm	2 – 3 nm	1 – 2nm	0.7 – 3.2 nm (1.7 nm)	-------

•Pt-particle size distribution of Model Catalyst A, after exposure to Lean-Rich cycles (240 s, 60 s) at 700°C (ADF STEM images of same sample area for all treatments)



•Fresh Sample

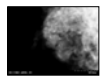
–Pt particles in 0.5 - 2.5-nm range



•After 4 hours

–Pt particles in 0.5 - 4.5-nm range

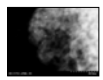
–Change in location



•After 8 hours

–Pt particles in 0.5 - 4.5-nm range but average increased by 0.4 nm

–No change in location



•After 12 hours

–Pt particles in 0.5 - 5.0-nm range

–No change in location

•After 16 hours

–No further change compared to 12 hour samples

Combining Theory and Experiments

Is it possible to examine computationally complex but experimentally simple systems by both theoretical and experimental methods?

- Forecast Improvements
- Optimize Performance

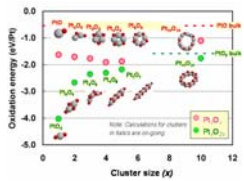
•Density Functional Theory Calculations

- Generalized gradient approximation (PW91 functional)
- Spin polarization to capture correct ground state
- Oxidation energy of Pt_xO_y clusters calculated as:

$$OE = (E_{cluster} - E_{Ptx} - \tfrac{1}{2}y \cdot E_{O2})/x$$

(1 eV ≈ 100 kJ/mol ≈ 23 kcal/mol)

- Convergence of results verified

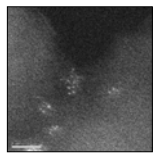


•Theoretical Model tells us that…

- Pure Pt clusters are easily oxidized; supported Pt nanoparticles should primarily be in oxidized forms in an oxidizing environment
- +4 oxidation state (i.e., Pt:O=1:2) is favored thermodynamically for Pt atoms
- Pt clusters have very different oxidation energetics and oxidized structures compared to the bulk phase
- Adsorption properties of O, O_2, and CO on Pt clusters are very different compared to an extended Pt surface
- Even small Pt oxide clusters are structurally complex, although patterns can be detected and may aid in future analysis

•Experimental Model Catalyst …

- Pt clusters on γ-alumina made of 10-15 atoms have been synthesized
- This cluster models theoretical calculations
- Theoretical calculations suggest that the Pt atoms should be oxidized



Aberration-corrected HA-ADF-STEM image of 2% Pt/γ-Al_2O_3

Publications

Narula C.K.; Daw S.; Hoard J.; Hammer T.;, "Materials Issues Related to Catalysts for Treatment of Diesel Exhaust," *Int. J. Amer. Ceram. Tech.*, (in press)
Xu, Y.; Shelton, W.A.; Schneider, W.F.;"Nanoscale Effects in the Reactivity of Pt Clusters towards CO oxidation," *19th North American Catalysis Society Meeting*, Philadelphia, USA, May 22-27, (2005)
Xu, Y.; Shelton, W.A.; Schneider, W.F.; "Theoretical studies based on Post-Hartree-Fock and DFT methods," *Synthesis and Applications of Oxide Nanoparticles and Nanostructures*, Rodriguez, J.A., ed.; John Wiley & Sons
Xu Y.; Shelton W.A.; Schneider W.F.; "Effect of Particle Size on the Oxidizability of Platinum Clusters, " *J. Am. Chem. Soc.*, (submitted)

Acknowledgement

This research was sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, U.S. Department of Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.